STRUCTURAL STUDIES OF POLYMERIC MATERIALS BY INFRARED SPECTROMETRY

BY

WILLIAM BORGEN TREUMANN

B. S., University of North Dakota, 1942

M. S., University of Illinois, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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STRUCTURAL STUDIES OF POLYMERIC MATERIALS BY INFRARED SPECTROMETRY

Certain differences in the structural features of synthetic rubber-like polymers are known to have pronounced effects on the physical and, to a lesser extent, the chemical properties of these polymers. Since the manner of polymerization affects the structure of the resulting product, it is important, both from a theoretical as well as a practical point of view, to develop satisfactory methods for the detection and measurement of these structural differences.

In the case of the polymers and copolymers of 1,3-butadiene, the manner in which the butadiene units are linked within the molecular chain is one such important structural feature. The presence of units of the 1,2- configuration has long been considered to be responsible for some of the undesirable characteristics of synthetic rubbers. Thus during recent years, the problem of estimating the degree to which 1,2- addtion has taken place in the polymerization of butadiene polymers has received considerable attention. The present study was undertaken with the object of developing a satisfactory infrared spectrometric method for the quantitative determination of the fraction of butadiene units which have undergone 1,2- addition in polybutadienes and butadiene-styrene copolymers.

In general, substances containing vinyl groups, including the polymers and copolymers of butadiene, exhibit marked absorption of infrared radiation at 910 cm^{-1}. The extinction coefficients at this wave number of three non-isomeric vinyl-group olefins were measured and found to be very nearly identical. The extinction coefficient at 910 cm^{-1} of the 1,2-butadiene units of the polymers and copolymers was assumed to be equal to that determined for the vinyl-group olefins. The extinction coefficient at this wave number of the 1,4-units was considered to be negligible, thus allowing the

computation of the vinyl group molarities of solutions of polybutadiene from the optical densities measured at 910 cm^{-1}. The ratio of the concentration of the vinyl groups to that of butadiene units in the solution examined was taken to be the fraction of such units having undergone 1,2-addition.

The extension of the method to butadiene-styrene copolymers required compositional analyses which were effected spectrometrically by the use of the 700 cm^{-1} band, characteristic of the phenyl group. This band was calibrated through optical density measurements of solutions of polystyrene. A correction was made for the contribution of the polybutadiene portion to the absorption at this wave number. The vinyl-group concentrations of the copolymer solutions were computed, as for the polybutadiene solutions, through the measurement of the optical densities at 910 cm^{-1}.

The values obtained for the percentages of 1,2- units are considered to be reproducible within one percentage point. Feasible methods of measuring the error introduced by the assumptions on which this method is based have not been developed, nor are there independent determinations of percentages of 1,2- units known to be of high accuracy. Hence it is not possible to estimate the probable error in the results obtained. It is considered, however, that if they are subject to systematic error they are likely to err positively.

Emulsion-polymerized polybutadienes which had been polymerized at different temperatures and under different condtions were found to have undergone between 20 and 24 per cent of 1,2- addition. Sodium-polymerized polybutadienes which had been prepared at various temperatures were found to have 70 to 71 per cent of their units in the 1,2-configuration. Thus although the degree of 1,2- addition is much higher for the sodium polybutadienes than for the emulsion polbutadienes, the variations in the degree of 1,2-addition within either major class of polybutadienes were found to be small.

Emulsion polymerized butadiene-styrene copolymers were found to have 20 to 22 per cent of 1,2- units in the polybutadiene portion; it is thus evident that the entrance of the styrene units into the polymeric chain had little or no influence on the structures acquired by the butadiene units.

Sodium polymerized butadiene-styrene copolymers were found to have much higher percentages of 1,2- units. Only two such polymers were analyzed; values of 65 and 72 per cent of 1,2- addition were obtained, respectively, for these polymers. The one having the lower percentage of 1,2- units had been polymerized at 30°C., the other at 50°C. Too few of these polymers have been examined to establish any correlation between the degree of 1,2- addition and polymerization temperature.

VITA

The author was born on February 26, 1916. He attended the city schools of Grand Forks, North Dakota. His education was continued at the University of North Dakota where he receievd the Bachelor of Science degree in 1942 and at the University of Illinois where he was granted the Master of Science degree in 1944.

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